

PYROLYSIS KINETICS OF VARIOUS AUSTRALIAN OIL SHALES IN NITROGEN AND CARBON DIOXIDE ATMOSPHERES

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ABSTRACT

The kinetics of oil generation from retorting of various Australian shales have been investigated under both nitrogen and carbon dioxide sweep gas conditions. Experiments were conducted both isothermally and nonisothermally with linear temperature control, in a unique fixed bed retorting system. The kinetics of these shales were directly compared with those of eastern and western U.S. shales, previously studied on the same experimental system.

The pyrolysis of the investigated Australian shales was found to comply with first-order global kinetics within the limits of experimental error. The activation energies calculated were: 217.2 kJ/gmole (CO_2) and 114.8 kJ/gmole (N_2) for Condor shale; 252.2 kJ/gmole (CO_2) and 190.1 kJ/gmole (N_2) for Rundle shale; 154.0 kJ/gmole (CO_2) and 127.4 kJ/gmole (N_2) for Stuart shale. The average Fisher assay of these shales are 62 cc/kg for Rundle, 63 cc/kg for Condor, and 100 cc/kg for Stuart shale.

INTRODUCTION

An experimental study has been performed in order to obtain the retorting kinetics of oil generation from various Australian Tertiary oil shales under both nitrogen and carbon dioxide sweep gas conditions. The carbon dioxide retorting has been investigated first by Lee et al. and proven efficient for the western U.S. type oil shale (1). Therefore, the rather nonconventional carbon dioxide retorting as well as the conventional nitrogen retorting has been applied to Australian shales.

The shale samples studied were taken from the Kerosene Creek member of the Stuart deposit, the Ramsey Crossing member of the Rundle deposit, and the Brown oil shale unit of the Condor deposit, all of which are located along the coastline of Queensland, Australia.

In order to obtain an unbiased comparison and to eliminate unaccountable systematic errors, a unique fixed bed retorting system was used to determine the kinetic parameters of each shale (2). Both the isothermal and nonisothermal retorting techniques were employed for the kinetic measurements, and the results compared favorably with each other. The pyrolysis of the Australian shales under investigation were found to comply with global first-order kinetics within the limits of experimental errors.

THEORY

Three experiments for each shale under different isothermal conditions were carried out and the global power-law type rate expression was applied to analyze the data:

$$\frac{dx}{dt} = A[\exp(-E/RT)](1-x)^n \quad (1)$$

where x is the kerogen conversion based on the Fisher assay oil yield, E is the activation energy, kJ/gmol, A is the Arrhenius frequency factor, 1/sec, and n is the reaction order.

The nonisothermal technique eliminated the uncertainty of the initial heat-up period which had been an inherent problem with a fixed bed type retorter for an isothermal measurement. The kinetic parameters were obtained for the condition that a linear heating rate be maintained. The choice of a linear heating rate is to facilitate an easier mathematical analysis. For an overall first-order reaction, one obtains the following equation by integration (1):

$$-\ln(1-x) = \frac{AE}{CE}[e^{-u}u^{-2} - 2e^{-u}u^{-3}] \quad (2)$$

where C is the heating rate (dT/dt) in $^{\circ}\text{C}/\text{min}$ and $u=E/RT$. Rearranging equation (2) yields

$$\frac{-\ln(1-x)}{T^2} = \frac{AR}{CE}[(1 - 2RT/E) \exp(-E/RT)] \quad (3)$$

Taking natural logarithms on both sides of equation (3) gives

$$\ln \frac{-\ln(1-x)}{T^2} = \ln \left(\frac{AR}{CE}(1 - 2RT/E) \right) - E/RT \quad (4)$$

A plot of $\ln[-\ln(1-x)/T^2]$ vs. $1/T$, which turns out to be a linear plot for $RT/E \ll 1$, gives the activation energy and the kinetic frequency factor for a first-order kinetics from the slope and intercept, respectively. The goodness of fit was a good indication of the validity of the assumed reaction order. A similar analysis can be done for an n -th order kinetics using successive approximation of exponential integrals and the best fitting order can be found by a regression technique (3).

EXPERIMENTAL SYSTEM AND PROCEDURE

A schematic diagram of the apparatus used for this study and a detailed design of retorter internals are published elsewhere (2). Some of the features of this retorting system are considered to be special or unique. These features include the use of a stainless steel wire mesh distributor plate, so that a well-defined fluid dynamic condition is achieved with a minimal pressure drop, the use of a quick opening and closing ball valve which permits the instantaneous loading of a sample in addition to permitting the application of both isothermal and nonisothermal techniques to the same retorter, introducing a chromel-alumel thermocouple directly into the shale bed to obtain good temperature control and measurements, and by connecting two specially designed graduated U-tubes in series which allows the condensable product to settle in the bottom of the tubes while the noncondensable product to pass through a bridge across the tube arms.

A 20 gram sample of -35+40 mesh Australian oil shale was used for each experiment. For an isothermal measurement the retorter was preheated to a temperature about 100 C higher than the reaction temperature to facilitate an easy and fast control of the temperature. For a nonisothermal measurement the retorter was heated up at a linear heating rate of 10 C/min, which was found to be ideal for kinetic measurement. The sweep gas was sent into the retorter at the nominally same temperature as the shale sample for both isothermal and nonisothermal measurement. The flow rate used was 2 cc(STP)/sec and is equivalent to the vapor hourly space velocities of 720 hour⁻¹. Since the length of the connecting line between the retorter and the collection tube was kept short and the temperature was kept high enough to keep the product as a vapor and the liquid holdup in the retort was negligible.

DATA AND ANALYSIS

Nitrogen Retorting Kinetic parameters for the pyrolysis of Australian and eastern and western U.S. oil shales, under nitrogen sweep gas conditions are summarized in Table 1. As shown in the table, the relative rates obtained from isothermal and nonisothermal methods are nearly the same at 450 C. However, the kinetic parameters obtained from nonisothermal retorting may give a more realistic set of engineering information of the overall kinetic parameters for the design of efficient and economical retorting processes, since it comes closer to actual retorter conditions. It should be noted that the lower relative reaction rate for North Carolina shale was due to the fact that the retorting of this shale required a much higher initial retorting temperature than those for the other shales studied. Therefore, the practical retorting temperatures under nitrogen sweep gas conditions ranges from 400 to 500 degrees Celcius for all three types of Australian shales which matches the practical retorting conditions of most of the western U.S. shales.

Table 1. Kinetic Parameters for Nitrogen Retorting of
Australian and Eastern United States Shales

Shale Type		Activation Energy, KJ/mol	Arrhenius Frequency Factor, (sec) ⁻¹	Relative Rates at 450°C
Rundle	N	190.09	4.17x10 ¹²	1.000
	I	180.89	9.10x10 ¹¹	1.008
Stuart	N	127.36	9.05x10 ⁷	0.739
	I	116.79	1.74x10 ⁷	0.825
Condor	N	114.83	9.92x10 ⁶	0.652
	I	104.08	1.94x10 ⁶	0.762
Ohio	N	170.62	3.54x10 ¹⁰	0.217
	I	185.32	3.53x10 ¹¹	0.187
West Virginia	N	203.11	5.74x10 ¹²	0.158
	I	201.37	5.74x10 ¹²	0.173
North Carolina	N	193.40	6.92x10 ⁸	1.50x10 ⁻⁵
	I	204.62	4.74x10 ⁹	1.01x10 ⁻⁴
Colorado	N	182.58	5.62x10 ¹¹	0.471

N denotes nonisothermal run

I denotes isothermal run

Table 2. Kinetic Parameters for Carbon Dioxide Retorting of
Australian and Eastern United States Shales

Shale Type		Activation Energy, KJ/mol	Arrhenius Frequency Factor, (sec) ⁻¹	Relative Rates at 450°C
Rundle	N	252.17	1.39×10^{17}	1.000
	I	243.33	3.48×10^{16}	1.090
Stuart	N	154.01	1.21×10^{10}	1.076
	I	141.02	1.61×10^9	1.243
Condor	N	217.24	5.92×10^{14}	1.422
	I	209.17	1.65×10^{14}	1.518
Ohio	N	141.23	4.45×10^8	0.332
	I	136.07	2.33×10^8	0.410
West Virginia	N	183.56	2.27×10^{11}	0.148
	I	178.32	1.11×10^{11}	0.173
North Carolina	N	211.37	8.43×10^9	5.38×10^{-5}
	I	202.91	2.13×10^9	5.55×10^{-5}
Colorado	N	189.96	6.89×10^{12}	1.548

N denotes nonisothermal run

I denotes isothermal run

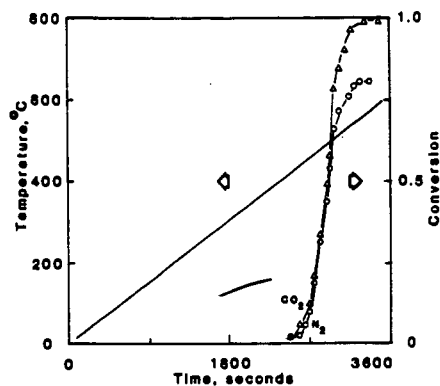


Figure 1.

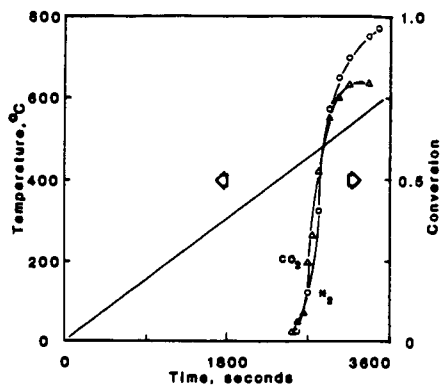


Figure 2.

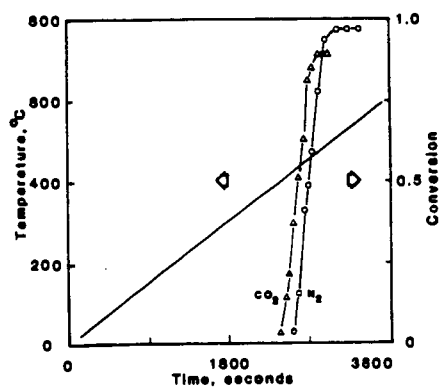


Figure 3.

Figure 1. Nonisothermal Kinetic Measurement of Stuart Shale under N_2 and CO_2 . -35+40 mesh; 10 $^{\circ}C/min$; 2 cc(STP)/sec.

Figure 2. Nonisothermal Kinetic Measurement of Rundle Shale under N_2 and CO_2 . (same conditions as Figure 1.)

Figure 3. Nonisothermal Kinetic Measurement of Condor Shale under N_2 and CO_2 . (same conditions as Figure 1.)

Carbon Dioxide Retorting Kinetic parameters for the pyrolysis of Australian and eastern and western oil shales under carbon dioxide sweep gas conditions are summarized in Table 2. Figures 1, 2, and 3 show the experimental data for nonisothermal kinetic measurement of pyrolysis of Stuart, Condor, and Rundle shales under nitrogen and carbon dioxide sweep gas conditions. It is interesting to note the difference in kinetic parameters between nitrogen and carbon dioxide retorting conditions. This is believed to be due to the difference in kerogen swelling in both gases and/or the differences in molecular penetration into pores between nitrogen and carbon dioxide. It has been known among the researchers that the kerogen in oil shale swells better in the carbon dioxide medium than the nitrogen medium. This is why carbon dioxide retorting is always kinetically faster than nitrogen retorting at nominally identical process conditions.

SUMMARY

The pyrolysis kinetics of various Australian oil shales were experimentally obtained using both isothermal and nonisothermal retorting techniques. The results from the two methods compared favorably with each other over a practical range of retorting temperatures. The pyrolysis reaction of the investigated Australian oil shales followed a global first-order kinetics very closely and the activation energies range from 110 to 250 kJ/gmole, depending on the type of shale. These values closely followed those for eastern and western U.S. oil shales retorted using the same experimental system. Every possible effort has been made to eliminate the internal and external mass transfer influence on the kinetics obtained, viz., using finely ground shales as well as providing optimal heat and mass transfer conditions.

In addition, the pyrolysis kinetics of various Australian shales were investigated both under nitrogen sweep gas conditions and under carbon dioxide sweep gas conditions and the results were directly compared. It was found that the carbon dioxide retorting process exhibits a kinetically faster rate of oil evolution from all the Australian shales. This result was true regardless of its impact on the overall yield from the shale and was equally valid for other types of oil shales including the Eastern and Western U.S. oil shales.

REFERENCES

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2. Joshi R. and Lee S., Liquid Fuels Technology, 1, 17, (1983).
3. Polasky M. E., ' Pyrolysis Kinetics and Process Optimization of Eastern United States and Australian Oil Shales ', Master's Thesis, The University of Akron, (1985).